NaSa CR-172,649

ECUT—BIOCATALYSIS RESEARCH ACTIVITY GENERATION OF CHEMICAL INTERMEDIATES BY CATALYTIC OXIDATIVE DECARBOXYLATION OF DILUTE ORGANIC ACIDS

By
S. Di Stefano
A. Gupta
J. D. Ingham

March 1983

California Institute of Technology
Jet Propulsion Laboratory
Pasadena, California

U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

NF00742

DISCLAIMER

This report has been reproduced directly from the best available copy

Available from the National Technical Information Service, U S Department of Commerce, Springfield, Virginia 22161

Price Printed Copy A02
Microfiche A01

Codes are used for pricing all publications The code is determined by the number of pages in the publication Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries *Energy Research Abstracts (ERA), Government Reports Announcements* and Index (*GRA* and I), *Scientific and Technical Abstract Reports (STAR),* and publication NTIS-PR-360 available from NTIS at the above address

ECUT

ENERGY CONVERSION AND UTILIZATION TECHNOLOGIES PROGRAM

Biocatalysis Research Activity

Generation of Chemical Intermediates by Catalytic Oxidative Decarboxylation of Dilute Organic Acids

S. Di Stefano, A. Gupta, and J.D. Ingham

March 1983

N83-25810#

ABSTRACT

Dilute streams of organic acids are byproducts of fermentation processes, paper and pulp industry waste streams, and processed urban waste. Currently, these are dumped since no method exists to extract the acids unless the streams are first concentrated. A catalytic process which would convert these dilute acids to useful chemicals such as alcohols and hydrocarbons would allow their utilization as a high volume non-fossil feedstock. The catalyst should cause loss of carbon dioxide from these dilute acids without heating to convert them to hydrocarbons which are not soluble in water and can be separated at high energy efficiency. A rhodium-based catalyst was prepared and preliminary experiments were completed where the catalyst appeared to decarboxylate dilute acids at concentrations of 1-10 vol%.

Electron spin resonance spectroscopy was used to characterize the catalyst as a first step leading toward modeling and optimization of rhodium catalysts. Also, a hybrid chemical/biological process for the production of hydrocarbons has been assessed. These types of catalysts could greatly increase energy efficiency of this process.

This Page Intentionally Left Blank

TABLE OF CONTENTS

SUMMARY

Dilute streams of organic acids are byproducts of fermentation processes, paper and pulp industry and processed urban waste. Currently, these are dumped since there is no method to extract the acids unless the streams are first concentrated. A catalytic process which would convert these acids to useful chemicals such as alcohols and hydrocarbons would open up their utilization as a high volume alternate, non-fossil feedstock of ~10^6 tons/year for the chemical industry, providing up to 10^{13} Btu's annually. Energy conservation at the quad level could be obtained by replacing petroleum-based feedstocks in new, more energy efficient hybrid chemical catalytic-biocatalytic processes.

The desired conversion pathway involves loss or expulsion of carbon dioxide from each molecule of the acid, i.e., decarboxylation to generate alcohols and hydrocarbons which are widely used as intermediates in the chemical industry. Currently there are no catalysts available for this process which can efficiently convert dilute acid streams, although Ce^{4+} promoted with I_2 slowly decarboxylates concentrated acids.

Previous studies have indicated that transition-metal catalysts and catalyst-modified electrodes can be developed that would be effective on dilute acid streams. Therefore, work was initiated at JPL to develop new catalysts for decarboxylation of acids in aqueous solutions.

Accomplishments to date include the preparation of rhodium-based catalysts for which preliminary qualitative experiments were conducted. The catalysts appeared to decarboxylate dilute acids at concentrations of 1-10 volume %; however, the results were not consistently reproducible at 1% concentration, and no kinetic measurements have been made. Further work is required to more completely define the catalyst systems, mechanisms, and practical limitations,

and to determine decarboxylation rates, yields, and susceptibilities to poisoning or inhibition.

The use of diagnostic techniques such as electron span resonance (ESR) spectroscopy and electrochemistry leading to some initial characterization of reactive intermediates in these systems has been examined. This type of characterization will lead to reactivity models which may be used to optimize the chemical structure of certain rhodium-based catalysts for the best turnover rate/stability trade-off.

Some novel hybrid chemical/biological processes for the production of hydrocarbon chemicals have been examined. An example of a hybrid process proposed by Levy, et al. (10) is conventional electrolysis (i.e., Kolbe synthesis) of dilute acid from a fermentation reactor. However, state-of-the-art technology would require about 5,000 Btu/lb or nearly 25% of the energy of the product for conversion of the acids to hydrocarbons. New catalyst systems could decrease the decarboxylation energy requirement to <2,000 Btu/lb of product by eliminating the most energy-intensive process steps, which are separation of the acids, and Kolbe electrolysis. The significance of this decrease in energy consumption is that it could increase the ratio of product energy/process energy for the overall hybrid process to approximately 10, compared with the value for conventional production of hydrocarbon fuel which has been estimated to be ~6. Thus, it should be practical to produce low molecular weight hydrocarbons from renewable resources with significantly less process energy consumption than for production from non-renewable petroleum.

2

I. INTRODUCTION

The conversion of organic carboxyl compounds to hydrocarbons has been known for a long time; Kolbe first studied the electrochemical oxidation of carboxylic acids to hydrocarbons in 1849, and since then, this topic has been the subject of numerous studies. More recently, a variety of transition metals have been reported as catalysts in the oxidative decarboxylation of carboxylic acids. The application of new catalysts and/or the development of catalyst modified electrodes for oxidative decarboxylation should ultimately give rise to highly efficient conversion processes. The goal of this research is to improve the understanding of the decarboxylation process by determining the mechanism of the decarboxylation reaction, and then optimize catalyst performance. Ultimately this understanding will be used to develop improved and less expensive efficient catalysts.

Improved efficiency would be obtained via new chemical catalytic systems (compared with conventional Kolbe electrolysis) because the overall energy efficiency of thermal catalytic processes is higher than electrolytic processes by a factor of more than two. It has already been shown by Levy, et al.[10], that the process:

$$\text{Biomass} \xrightarrow{\text{Fermentation}} \text{Carboxylic Acids}$$

$$\text{Carboxylic Acids} \xrightarrow{\text{Kolbe Electrolysis}} \text{Hydrocarbons}$$
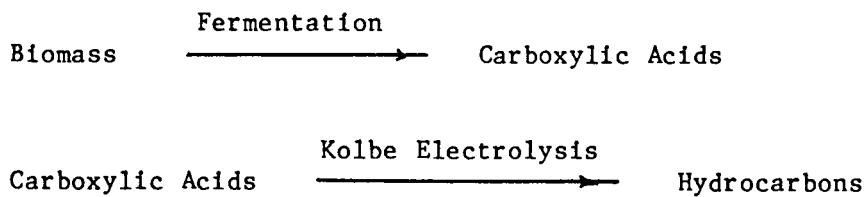
is energy efficient, giving rise to a favorable energy balance of ~4.0/1.0 (product energy/process energy). This means that processing of the carboxylic acids consumes approximately 25% of the total product energy.

Organic fatty acids are major components of byproducts of pulping operations in paper manufacture and allied industries, the third largest energy user of the major industry groups[1]. This technology can result in more efficient energy use in this industry and in the recovery and conversion of fatty acids which are components of anaerobic digestion of biomass and organic waste materials. Development of more efficient catalysts for oxidative decarboxylation could ultimately result in new hybrid chemical and fuel production processes that would result in energy consumption reduction at the quad level.

II.   BACKGROUND

a.   Homogenous Transition Metal Catalyzed Oxidative Decarboxylation

Certain oxidants such as Ce^{4+} and Mn^{3+} oxidize carboxylic acids _via_ a one electron oxidation process. This process is slow at room temperature but may be promoted by addition of I_2 or strong acids. Scheme I outlines the mechanism for oxidative decarboxylation using Mn^{3+} [2]. This mechanism involves formation of hydrocarbon radical intermediates. Formation of energetic radicals as intermediates requires that the overall reaction have a large activation energy. Energetic transients tend to result in the formation of a mixture of products, including alcohols and hydrocarbons. Once the radical intermediates are formed, it is difficult to control their reactivity.

4

$$Mn^{3+} + RCO_2H \longrightarrow Mn^{3+} O_2CR + H^+$$

$$Mn^{3+} O_2CR \longrightarrow Mn^{2+} + R\cdot + CO_2$$

$$R\cdot \longrightarrow R - R$$
$$R\cdot \xrightarrow{\;SH\;} RH + S\cdot \text{ etc.}$$

$$Mn^{3+} + R\cdot \longrightarrow Mn^{2+} + R^+_{ox}$$
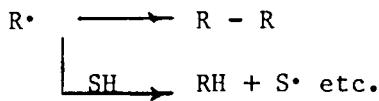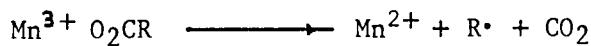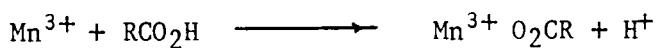
Scheme 1

In order to avoid these problems, we propose to investigate non-radical pathways to decarboxylation. Suitable transition metal catalysts will be developed which can act as templates for this process.

Thermodynamic data for certain reactions of interest are given below.

Table 1

|			
CH_3COOH	$\longrightarrow$	$CH_4 + CO_2$	$\Delta H \simeq -8.2$ kcal/mole
CH_3COOH	$\longrightarrow$	$CH_3OH + CO$	$\Delta H \simeq +21.2$ kcal/mole
CH_3COOH	$\longrightarrow$	$H_2O + H_2CO$	$\Delta H \simeq +33.6$ kcal/mole
$CH_3COOH + 1/2 \; O_2$		$CH_3OH + CO_2$	$\Delta H \simeq -46.5$ kcal/mole

The reaction of interest which proceeds with a small exothermicity (and hence, minimum loss of energy in the form of heat) is the formation of hydrocarbon and carbon dioxide. Although methane is not the desired product (because of its relatively low value as a chemical intermediate) it will be used in this work as a model product since its formation from acetic acid in high yield

would indicate that a non-radical pathway is operative. The applicability of these catalysts for production of higher hydrocarbons (such as ethane or pentane) will be determined in subsequent work.

Three possible non-radical pathways to decarboxylation can be proposed.

b.   Non-Radical Decarboxylation Via Extrusion/Insertion

One potential mechanism is $\underline{via}$ extrusion/insertion:

$$CH_3COOH + M^{n+} \longrightarrow M - OOCCH_3^{(n-1)+} + H^+$$

$$CH_4 + M^{n+} \xleftarrow{\quad H+ \quad} [M - CH_3]^{(n-1)+} + CO_2$$
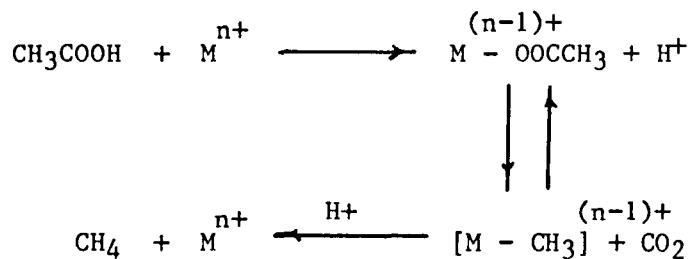
However, known examples of CO_2 insertion and extrusion are rare in the literature. For example, insertion of CO_2 into a metal diallylamide turns out to be catalyzed by free amine implying a pre-equilibrium, where L_nM is a coordinated metal center:

$$R_2NH + CO_2 \rightleftharpoons R_2NCOOH$$

$$L_nM - NR_2 + R_2NCOOH \rightleftharpoons L_nM - O_2CNR_2$$
$$+ R_2NH$$
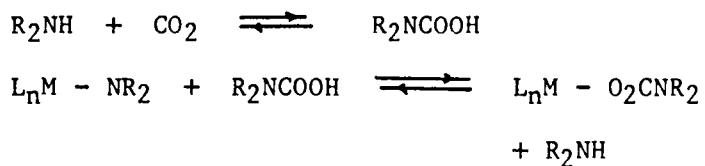
Similarly, the reaction reported by English et al.[3]

$$Ir^I + CO_2 + CH_3CN \longrightarrow H - Ir - O_2C - CH_2CN$$
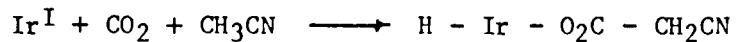
does not involve insertion of CO_2 into $H - Ir - CH_2CN$.

Although existing evidence for extrusion of CO_2 is weak, our preliminary results encourage us to attempt to design specific metal complexes capable of CO_2 extrusion.

c.   Non-Radical Decarboxylation Via Oxidative Addition

Oxidative addition may also be proposed:

$$CH_3COOH + M \longrightarrow M \begin{array}{c} \nearrow H \\ \searrow CH_2COOH \end{array}$$

$$M + CH_4 \xleftarrow{\quad H^+ \quad} M \begin{array}{c} \nearrow H^- \\ \diagdown\!\!\diagdown CH_2 \end{array} + CO_2 + H^+$$
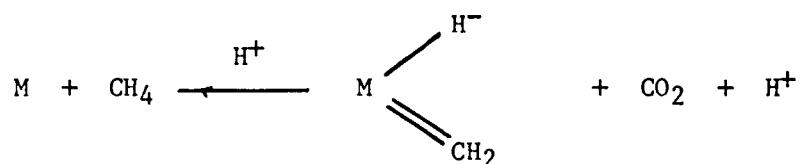
The "Carbene" Mechanism

There is some precedence for the possibility of oxidative addition across CH-bonds, exemplified by Shilov[4]. In particular, $PtCl_2$ in aqueous CH_3COOH is a good catalyst for alkane H-D exchange, and the methyl group in acetic acid has been noted to undergo extensive deuteration under the reaction conditions. However, basic conditions may be necessary and an early transition metal catalyst such as Nb or Ti may be more suitable, since carbenes seem to be more common for these metals.

d.   Indirect Oxidative Addition

The Monsanto process for synthesis of acetic acid is:

$$CH_3OH + CO \longrightarrow CH_3COOH, \quad \Delta H = -21.2 \text{ kcal/mole}$$

7
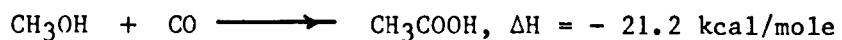
catalyzed by rhodium iodocarbonyl and believed to proceed via two equilibria:

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$

$$CH_3COOH + HI \longrightarrow CH_3COI + H_2O .$$
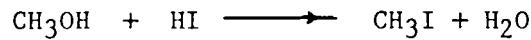
The alkyl and acyl iodides are both facile oxidative addends (as CH_3COOH is not), so the following equilibria are set up in the presence of Rh^I:

$$Rh(I) + CH_3I \longrightarrow Rh^{III} \Big\langle {}^{CH_3}_{I} \xrightarrow{CO} Rh^{III} \Big\langle {}^{COCH_3}_{I}$$

$$\updownarrow$$

$$Rh^I + CH_3COI$$
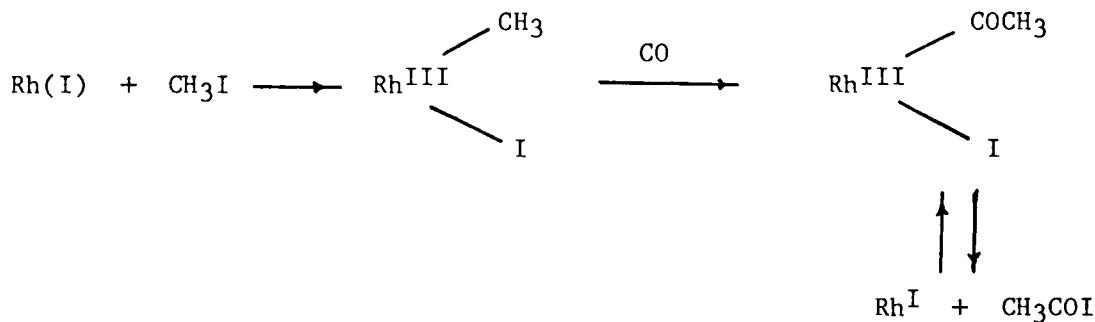
Theoretically, if it were possible to remove CO from the system by starting with excess acetic acid, it would be possible to drive methanol formation from acetic acid. A rhodium (I) phosphine complex should be better tha $Rh(CO)_2 I_2$ for this purpose [5] or perhaps a heterogenous catalyst such as rhodium on zeolites (6). It might also be possible to intercept the methyl complex:

$$Rh^{III} \Big\langle {}^{CH_3}_{I} \xrightarrow{H^+} CH_4 + Rh^{III} - I$$
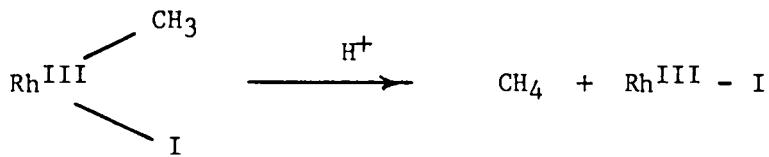
Turning CO from acyl elimination into CO_2 and regenerating Rh(I) now simply amounts to the water gas shift reaction:

$$Rh^{III} -_{\textbf{.}} I + CO \longrightarrow Rh^{III} \Big\langle {}^{CO}_{I} \xrightarrow{H_2O} Rh^I + CO_2$$
$$+ I^- + 2H^+$$
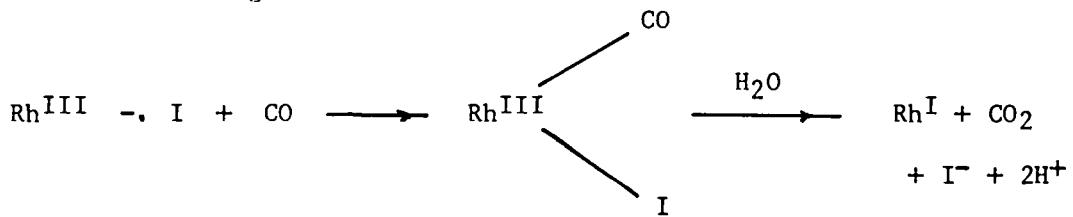
III. PROGRESS

a. Homogeneous Systems Using Rh-Isonitrile Complexes

In previous work, we have investigated the reaction of carbon monoxide and other substrates with the inorganic complex $Rh_2(bridge)_4^{2+}$, where the bridge is α, ω-diisonitrilo propane. In aqueous solution, in the presence of an oxidant such as O_2, $Rh_2(bridge)_4^{2+}$ is oxidized to a stable tetrameric form, $Rh_4(bridge)_8^{6+}$. This complex, hereafter abbreviated Rh_4^{6+}, contains a linear chain of four rhodium nuclei. Upon the replacement of air by an atmosphere of H_2, Rh_4^{6+} is partially reduced with corresponding oligomerization to form an insoluble black polymer. The polymer can be reoxidized to the tetrameric form by the reintroduction of air or by pumping off H_2.

If CO is used instead of H_2, the same qualitative behavior is observed:

$$Rh_4^{6+} \xrightarrow[25°C]{CO} (Rh_4^{4+})n \text{ black polymer} \xrightarrow{air} Rh_4^{6+} + CO_2$$
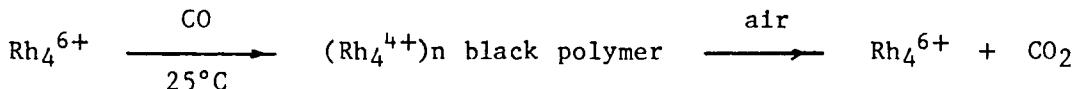
In this case, CO_2 is observed as a product and the polymer cannot be returned to the tetramer by pumping off CO. When re-exposed to air, the regeneration of Rh_4^{6+} is quantitative. Thus, it appears that the following overall reaction is taking place:

$$CO + 1/2\ O_2 \xrightarrow{Rh_4^{6+}} CO_2$$
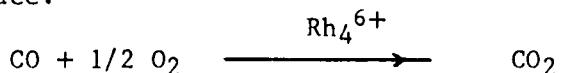
The Rh_4^{6+} solution may be cycled many times without apparent loss of the characteristic absorption spectrum.

In the presence of acetic acid (10% V/V) with Rh_4^{6+} removal of oxygen causes the same black precipitate to occur. Gas is evolved which is most likely CO_2. Upon re-exposure to air, Rh_4^{6+} is quantitatively regenerated. As

9

in the case of CO, the solution may be cycled many times by alternate degassing and aeration of the sample with no apparent loss of catalyst. GCMS analysis of the product mixture showed that simple hydrocarbons (e.g., CH_4) are formed in addition to CO_2. Isotope labelling experiments using CH_3COOH produced labelled CO_2 qualitatively. However, quantitative kinetic data have not yet been obtained.

To accomplish decarboxylation by a non-radical, template pathway, a heterogenous catalyst system might be more appropriate (vide supra). To this end we synthesized a two-dimensional coordination polymer of Rhodium(I). The polymer is of the type $[Rh-(bridge)_2^+ Cl^- \cdot x H_2O]_n$ (bridge = 1,4-diisocyanobenzene), and consists of colinear bridging ligands separating Rh nuclei by 12Å, forming a one-dimensional planar array. These arrays are stacked in an eclipsed manner giving an intermetallic distance of 3.31Å, only slightly longer than those of dinuclear cations [7] (i.e., Rh_4^{6+} described above for homogenous catalysis). See Figure 1.

This polymeric rhodium network polymer is a semiconductor material (k $\sim 10^{-6} \Omega^{-1} cm^{-1}$) and shows promising properties for catalysis and photocatalysis. The new two-dimensional Rh(I) polymer is found to be more stable than the homogenous Rh(I) dinuclear cations. Preliminary experiments in which the Rh(I)-polymer reacts with 1% V/V acetic acid indicate the evolution of CO_2 and there is also evidence of hydrocarbon products from mass spectral data. However, in some cases, CO_2 evolution higher than that attributed to the CO_2 background was not observed, which indicates the possibility of catalyst inhibition (or poisoning) by unknown components. Further work is required to define the mechanisms and practical limitations of this catalyst and to determine decarboxylation rates, yields, and susceptibility to poisoning or inhibition.
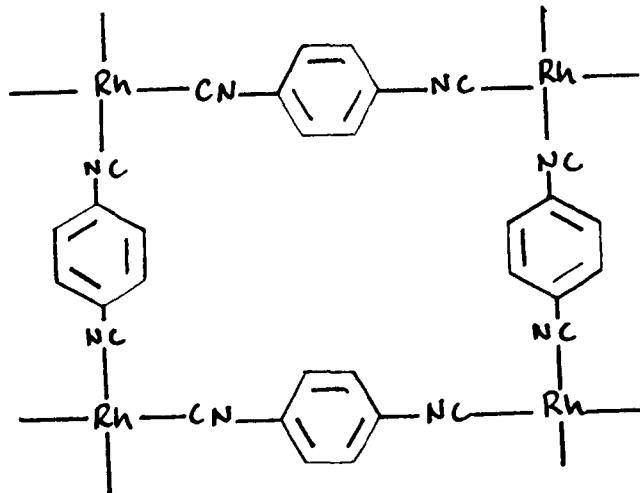
Figure 1.   Two-Dimensional Model of [Rh(bridge)$_2$]
Network Polymer.

b.   Characterization of the Electronic Structure of the Catalytic Sites by
ESR Spectroscopy

The electron paramagnetic resonance of a model compound (i.e., rhodium
trifluroacetate dimer) was recently determined[8]. This compound is a dimer
of two Rh(II) atoms (d^7 configuration) with four trifluroacetate ligands in a
square planar arrangement. Since this compound is diamagnetic, the spectrum
was studied as a nitroxide spin adduct. The M.O. diagram consistent with the
ESR spectrum is shown in Figure 2 [8].

In its fully reduced state, the rhodium atoms in the rhodium polymer are
formally in the +1 oxidation state. However by analogy to the mixed oxidation
state of the rhodium isonitrile dimers, there are a number of mixed valence
sites in the rhodium polymer. Futhermore, it is probably the sites with a
mixed oxidation state that are responsible for the catalytic activity. A
quantitative measure of the number of catalytic sites can be obtained by using
ESR spectroscopy, since a combination of Rh(I)-Rh(II) sites will result in an
unpaired electron and hence an ESR signal. The ESR spectrum of a sample of

$$\sigma^* \quad\underline{}\quad 1/\sqrt{2}(d^1_{z^2} - d^2_{z^2})$$

$$\pi^* \quad\begin{array}{l}\underline{}\; {}^{\nearrow}1/\sqrt{2}(d^1_{xz} - d^2_{xz}) \\ \underline{}\; {}^{\searrow}1/\sqrt{2}(d^1_{yz} - d^2_{yz})\end{array}$$

$$\delta^* \quad\underline{}\quad 1/\sqrt{2}(d^1_{xy} - d^2_{xy})$$

$$\delta \quad\underline{}\quad 1/\sqrt{2}(d^1_{xy} + d^2_{xy})$$

$$\pi \quad\begin{array}{l}\underline{}\; {}^{\nearrow}1/\sqrt{2}(d^1_{xz} + d^2_{xz}) \\ \underline{}\; {}^{\searrow}1/\sqrt{2}(d^1_{yz} + d^2_{yz})\end{array}$$

$$\sigma \quad\underline{}\quad 1/\sqrt{2}(d_{z^2} + d_{z^2})$$
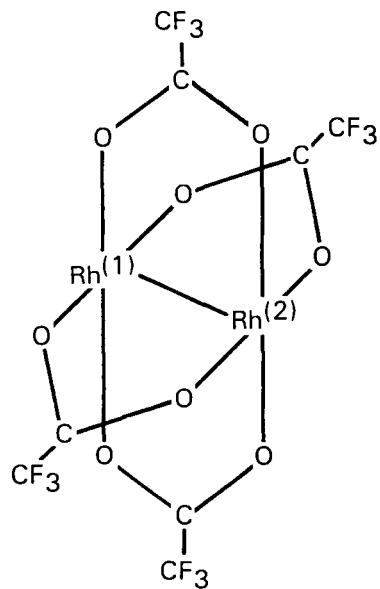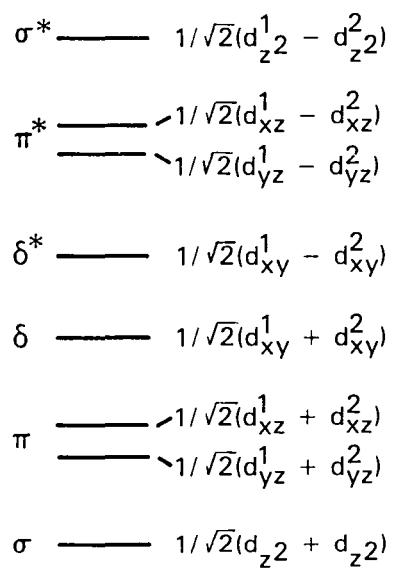
Figure 2. Qualitative M.O. Diagram for Rh(II) Dimer.

[Rh (bridge)$_2^+$ Cl$^-\cdot$ H$_2$O]$_n$ (bridge = 1,4'diisocyanobenzene) is shown in Figure 3. In this figure, traces A and B are duplicate traces of identical samples of Rh-polymer. The two spectral features are assigned to the hyperfine splitting components G$_{||}$ and G$\underline{\perp}$ of ^{103}Rh (I = 1/2), and are consistent with an unpaired electron in an orbital of σ symmetry. Trace C is the spectrum of the Rh-polymer after having reacted with acetic acid; the decrease in intensity can be accounted for by a decrease in the number of active sites Rh(I)-Rh(II) due to reduction of the active centers in the decarboxylation reaction. Quantitative measurements of the intensity change will lead to a direct method for monitoring catalytic activity.
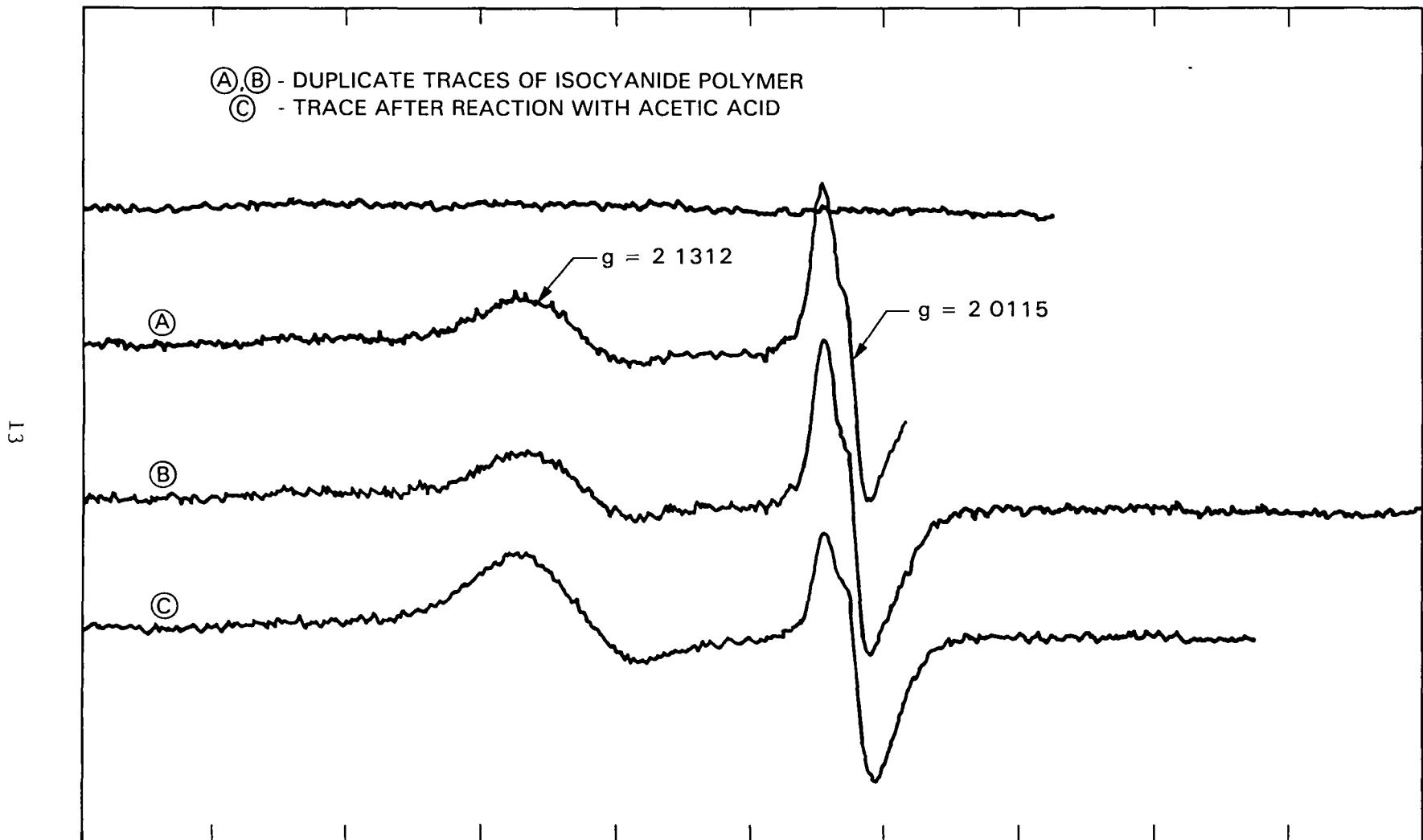
Figure 3. ESR Spectra of Isocyanide Network Polymer.

13

c. Electrochemical and Electrocatalytic Oxidative Decarboxylation

Generally speaking, electrodes act as catalysts and all electrochemical reactions might be viewed as heterogenous catalytic processes under the influence of imposed electric fields. Electrodes have different catalytic activity depending on the electrode material, the surface morphology and the treatment of the electrode. The most widely studied electro-organic reaction is the oxidative decarboxylation of carboxylic acids (Kolbe electrolysis). The Kolbe reaction is usually carried out in solutions of alkali metal salts of carboxylic acids at platinum anodes. The reaction proceeds preferentially as follows:

$$2 \; RCO_2^- \xrightarrow{-2e^-} 2R\cdot \; + \; 2CO_2$$

$$2R\cdot \longrightarrow RR$$
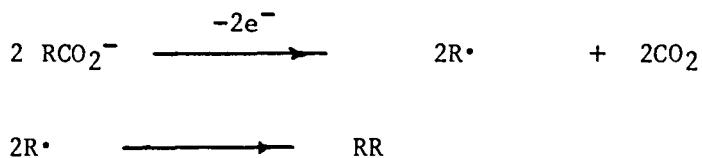
The mechanistic pathway depends on several parameters such as anode material, pH, nature of medium and concentration of carboxylic acid. Products by both carbonium ion and radical ion mechanisms can be obtained depending on the conditions[9]. Kolbe electrolysis has been used as a final step in the development of a process for the conversion of liquid fuels from biomass. A favorable energy balance (product energy/process energy) of about 4.0/1.0 has been estimated for this process[10]. This energy balance could be further increased by application of the photo-Kolbe process. This modification would consist of utilizing an anode of an appropriate semiconductor material, and solar radiation as part of the driving force for the decarboxylation reaction. Bard has shown that for $n-TiO_2$ anodes, the photo-Kolbe oxidative decarboxylation of acetic acid can occur with a quantum efficiency $\sim65\%$ [11]. The electrolytic process can also be made more efficient by the use of

chemically modified electrodes. In this case, the electrode surface is coated with a thin film of catalyst, and to the extent that the film allows the passage of current, the catalytic reaction proceeds at the surface of the catalyst. Preliminary cyclic voltametric experiments where the [Rh (bridge)$_2^+$ Cl$^-$· x H$_2$O]$_n$ polymer was coated on graphite electrodes show several oxidation reduction peaks in the range between 0 to +1.8V vs. SCE. The peaks are consistent with one electron oxidation reduction of mixed Rh(I)-R(II) species[12]. This type of electrode modification can lead to the in situ regeneration of the catalytic substance:

$$[Rh(I)-Rh(II)]-Polymer + RCO_2H \xrightarrow{+e^-} R\cdot + CO_2 + H^+ + [Rh(I)-Rh(I)]-polymer$$

Then at the anode:

$$[Rh(I)-Rh(I)]-Polymer \xrightarrow{-e^-} [Rh(I)-Rh(II)]-polymer$$
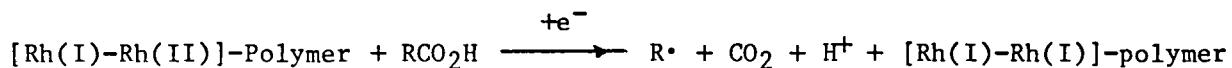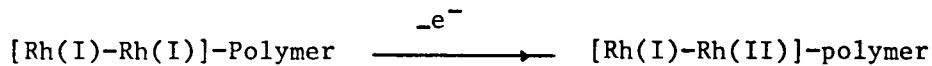
Additional energy savings could then be realized for an electrolytic process based on this system since minimal recovery of spent catalyst would be required.

Another electrocatalytic hybrid scheme which looks very promising is the electrochemical regeneration of enzymatic cofactors. Recently [13] a procedure has been developed in which the regeneration of NAD(P)H from NAD(P) is accomplished by the electrochemical reduction of oxidized to reduced methyl viologen ($MV^{+2} \rightarrow MV^{+1}$) followed by flaudenzyme catalyzed reductions of the nicotinamide cofactor by this MV^{+1}. This combined electrochemical enzymatic scheme is more convenient than classical methods and gives rise to much higher turnover numbers. This scheme is schematically shown in Figure 4.
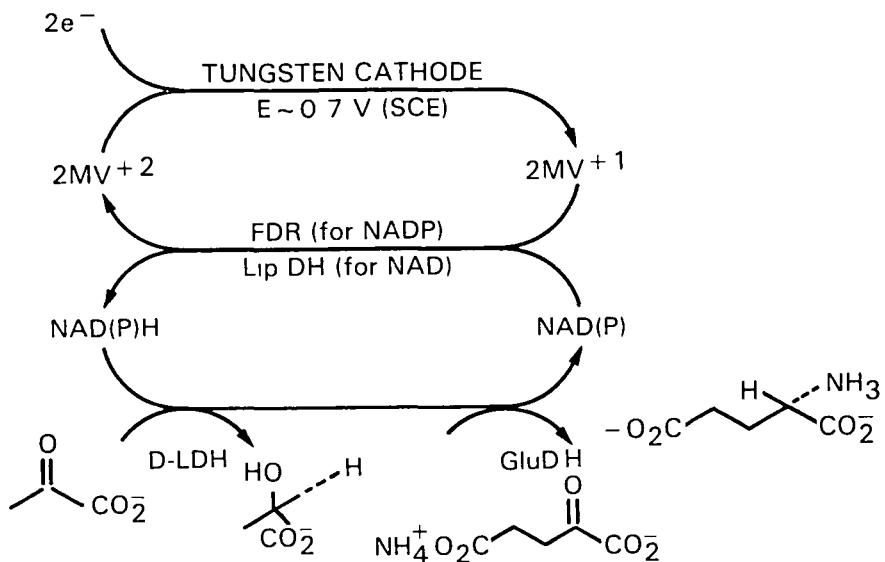
Figure 4. Electrochemical Regeneration of NAD(P)H from Ref. 13.

MV ≡ Methyl viologen; FDR ≡ ferredoxin-NADP reductase

LipDH ≡ lipoamide dehydrogenase; D-LDH ≡ D-lactate

dehydrogenase; GLuDH, ≡ glutamic dehydrogenase

d.   Potential for Increased Energy Efficiency of Hybrid Processes

It has been estimated that energy consumption expressed as the ratio of product energy to process energy for ethanol production by fermentation is 0.65 [10] to about 1.8 [14], depending on assumptions used in the analysis. This ratio is a reasonable measure of energy consumption because it indicates that if the product was burned as fuel, there would be no net energy benefit if the ratio is one or less. Furthermore, it provides a measure that can be

compared with hydrocarbon production from petroleum, where the ratio is approximately six [14].

For the hybrid biocatalytic-chemical process for production of hydrocarbon previously proposed and investigated [10] the ratio is about four. Essentially all of the process energy is utilized to separate the carboxylic acids and then convert them to hydrocarbons by Kolbe electrolysis. A comparison of this process with an advanced process that would be based on utilization of wood and waste, and advanced biocatalyst and chemical catalyst systems is shown in Figure 5. The values for energy consumption were estimated as follows. Energy for wood/waste production or collection was assumed to be 50% of the energy required for corn production. The net process energy for enzymatic hydrolysis and fermentation was zero, based on an analysis by Chem Systems, Inc. [15] for n-butanol production. The total energy for decarboxylation using a new catalyst was estimated to be 2000 Btu/lb, but could be less, depending on reactor conditions and process constraints.

The significance of this estimate is that it shows that advances in catalysts could yield energy benefit ratios that are more favorable than for hydrocarbons from non-renewable resources, and the ratios would be much higher than previously estimated values for ethanol production. The ratios (product energy/process energy) are: ethanol by fermentation, 0.7 to 1.8; hydrocarbons by fermentation and Kolbe electrolysis, 4.0; hydrocarbons from petroleum, ~6.0; and hydrocarbons by fermentation, using advanced catalysts, >10.2. An additional advantage of such a process is that most of the existing infrastructure and process operations for conversion of hydrocarbons to other chemicals could be effectively utilized.

PROCESS ENERGY

2500 BTU/LB* (CONSUMED)	0 BTU/LB (NET)	5100 BTU/LB (CONSUMED)	20,500 BTU/LB (PRODUCED)
FEEDSTOCK- CORN PRODUCTION	FERMENTATION TO CARBOXYLIC ACIDS	ACID SEPARATION AND KOLBE ELECTROLYSIS	HYDROCARBON PRODUCTS
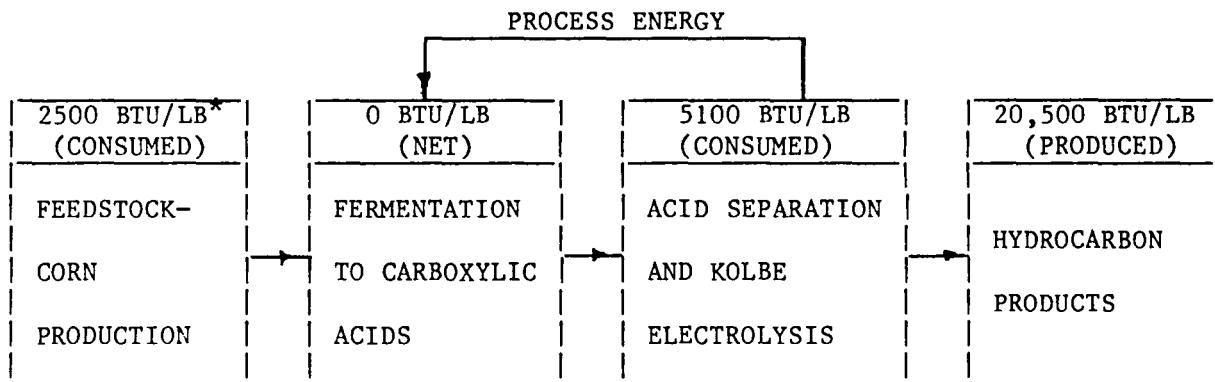
A. PREVIOUSLY PROPOSED PROCESS (BY LEVY, ET. AL.)

1250 BTU/LB (CONSUMED)
FEEDSTOCK WOOD/WASTE PRODUCTION/ COLLECTION

PROCESS ENERGY

EXCESS BTU/LB (PRODUCED)	0 BTU/LB (NET)	<2000 BTU/LB (CONSUMED)	20,500 BTU/LB (PRODUCED)
ENZYME CONVERSION: NEW BIOCATALYSTS	FERMENTATION TO CARBOXYLIC ACIDS - NEW BIOCATALYSIS	DECARBOXYLATION WITH NEW CHEMICAL CATALYST	HYDROCARBON PRODUCTS
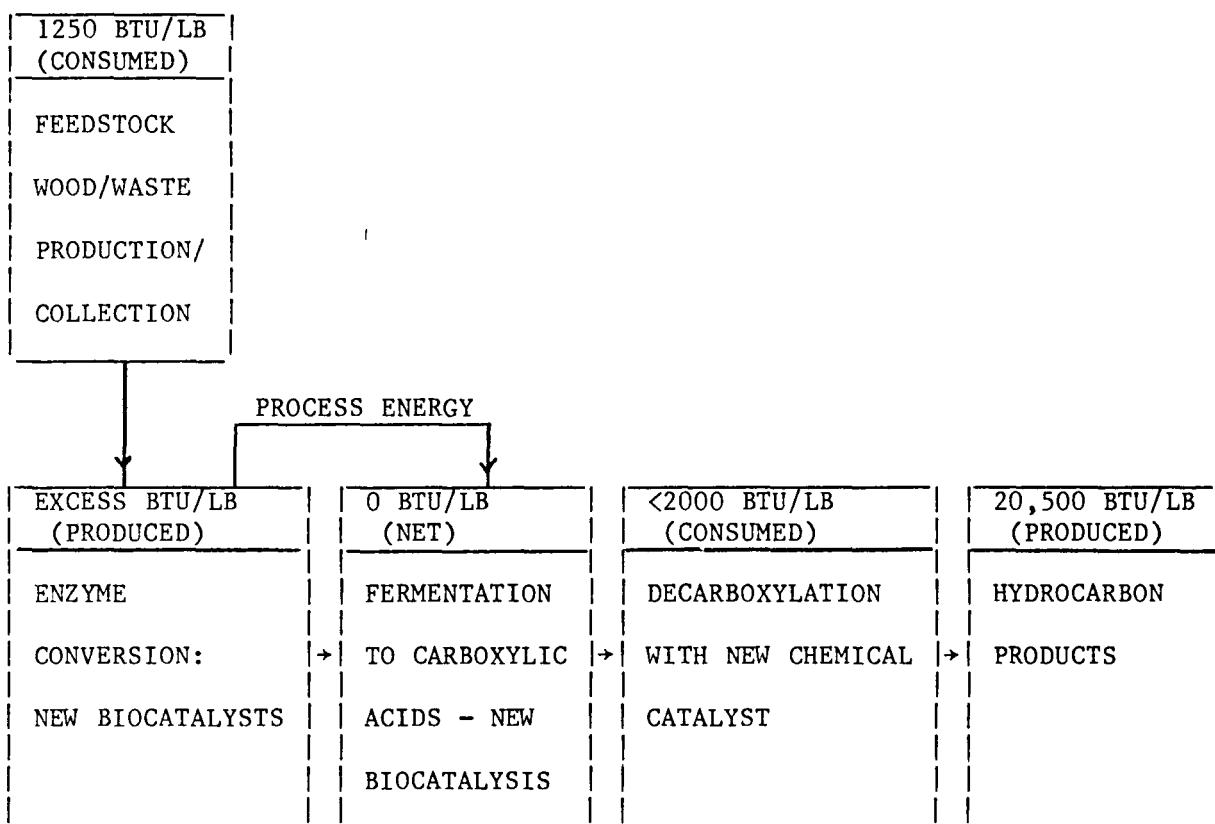
B. ADVANCED CATALYTIC PROCESS

A. { Ratio of Product Energy: Total Energy Used = 2.7;
     Ratio of Product Energy: Process Energy = 4.0.

B. { Ratio of Product Energy: Total Energy Used > 6.3;
     Ratio of Product Energy: Process Energy > 10.2.

* Per pound of final product

Figure 5.   Comparison of Hybrid Processes.

18

IV. REFERENCES

1. Bodine, J.F., et. al., "Industrial Energy Use Data Book", Oak Ridge Associated Universities, ORAU-160, Oak Ridge, Tennessee, 1980.

2. Kochi, J.K. and Anderson, J.M., J. Am. Chem. Soc. 92, 2450 (1970).

3. English, A.D. and Hershovite, T., J. Am. Chem. Soc. 99, 1648 (1977).

4. Shilov, A.E., Pure and Appl. Chem., 50, 725 (1978).

5. Doughty, D.H. and Pignolet, L.H., J. Am. Chem. Soc. 100 7083 (1978).

6. Scurrell, M.S. and Christensen, B., J. Chem. Soc. Faraday I, 2036 (1977).

7. Efraty, A., et. al., J. Am. Chem. Soc. 102, 6341 (1980).

8. Drago, R.S., et. al. J. Am. Chem. Soc. 99, 1055 (1977).

9. Kyriacou, D.K., "Basics of Electro-organic Synthesis", John Wiley and Sons, New York, 1981.

10. Levy, P.F., Sanderson, J.E., and Wise, D.L., "Biotechnology and Bioengineering Sym. No. 11", pp. 239, John Wiley and Sons, New York, 1981.

11. Bard, A.J. and Kraeutler, B., J. Am. Chem. Soc. 99, 7729 (1977).

12. Mann, K.R. and Parkinson, B.A., Inorg. Chem. 20, 1921 (1981).

13. Whitsides, G.M., et. al., J. Org. Chem., 46, 4622 (1981).

14. Hopkinson, Jr., C.S. and Day, Jr., J.W., Science, 207, 302 (1980).

15. Chem Systems, Inc., "Technical and Economic Assessment of Processes for the Production of Butanol and Acetone", prepared for the Jet Propulsion Laboratory, Energy Conversion and Utilization Technology (ECUT) Program for the U.S. Department of Energy, September, 1982.

End of Document